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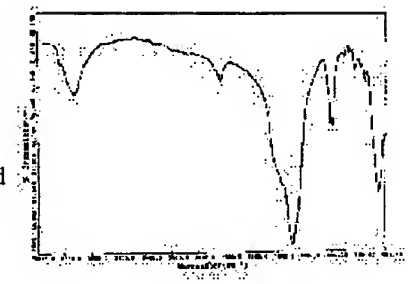
(54) SCALY LOW CRYSTALLINE SILICA AND ITS PRODUCTION

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a scaly low crystalline silica harmless to a human body, excellent in reactivity on the surface useful as a filler for cosmetic, antiperspirant, pack agent, coating material or resin and for various carriers and to provide a method for producing the silica.
SOLUTION: This scaly low crystalline silica has 0.001-1 μm thickness, 10 ratio (aspect ratio) of the longest length of the scaly plate to the thickness, ≥3 ratio of the shortest length of the scaly plate to the thickness, <10% measured value of crystal type free silicic acid by X-ray diffraction a nalysis and silanol group absorptions at 3,600-3,700 and 3,400-3,500 cm-1 of IR spectrum. This method for producing the silica comprises dealkalizing an aqueous solution of a silicic acid to give a silica sol and subjecting the sol to hydrothermal treatment.



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* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] While this invention is harmless to a human body, it is excellent in surface reactivity and relates to the low crystallinity silica and its manufacture method of the shape of a scale which can be used suitable for uses, such as fillers, such as a charge of makeup, an antiperspirant, a pack agent, a paint, or a resin, and chromatography support, a catalyst support.
[0002]
[Description of the Prior Art] Conventionally, the crystalline-substance silica in the meaning that a peak comes out by the X diffraction called so-called silica X is known (Beitr.Mineral.Petrogr.10,242-259 (1964)).
[0003] Although these are the forms to which many scale-like particles adhered, it is the quality of nonporous and is lacking in reactivity, and a substance top is difficult for making this support the specific matter or using it for it as a filler.
[0004] Moreover, crystalline silicas, such as a quartz and a cristobalite, are the silicosis whose medical treatment deposition is carried out to a lung and its circumference organization, and is a difficult illness when it is classified into crystallized type isolation silicic acid and is inhaled by **** as dust for a long period of time (Silicosis). Also pathologically the cause and bird clapper to cause are checked and are regulated in a black lung method or black lung method enforcement regulations on the occupational-safety-and-health side. Although amorphous silicas, such as ******** and silica gel, are classified into amorphous mold isolation silicic acid, it is known that possibility of comparing an amorphous mold with a crystallized type and causing silicosis is also remarkably small (fine particles, industry, 10, 25-40 (1980)).
[0005] It is the name distinguished from the joint silicic acid which constitutes silicate, and silicon has combined only with oxygen in three dimensions, other elements are in the state which has not been combined, and, in short, isolation silicic acid is a silicon dioxide (Si O2). It means. Although such isolation silicic acid is classified into an above-mentioned amorphous mold, an above-mentioned crystallized type, etc., a fixed quantity is possible for the crystallized type isolation silicic acid used as the cause which causes silicosis by the analyzing method etc.
[0006]
[Problem(s) to be Solved by the Invention] The purpose of this invention is excellent in properties, such as spreading nature, a stacking tendency, and concealment nature, in order to make a scale-like form, and it has enough few amounts of detrimental crystallized type isolation silicic acid from the field of an occupational safety and health, and is to offer the new scale-like silica of low crystallinity which has further the reactant high basis in which chemical modification is possible on a front face, and its manufacture method.
[0007]
[Means for Solving the Problem] This invention persons by carrying out hydrothermal processing of the start raw material containing the source of a silica, and the source of alkali, as a result of inquiring wholeheartedly in view of the importance of the above-mentioned technical problem Preferably to that the sufficiently few scale-like low crystallinity silica of the content of crystallized type isolation silicic acid detrimental to a human body is obtained, and a pan Thus, it finds out that what has the silanol group which is a scale-like low crystallinity silica and has an absorption band in the specific field of an IR spectrum is obtained, and came to complete this invention.
[0008] Namely, the above-mentioned technical problem of this invention consists of a scale-like board whose (1) thickness is 0.001-1 micrometer. The ratio (aspect ratio) of the longest length of this scale-like board to this thickness is the silica of the shape of a scale in which the ratio of the minimum length of this scale-like board to at least 10 and this thickness has at least 3. And the scale-like silica of low crystallinity characterized by the measured value of the crystallized type isolation silicic acid by the analyzing method being less than 10%, And therefore, the manufacture method of the scale-like silica of low crystallinity given in (1) which uses as a start raw material the silica sol obtained by carrying out dealkalization of the (2) silicic-acid alkali solution, carries out hydrothermal processing of this silica sol, and is characterized by the bird clapper is solved.
[0009] That is, if this invention is followed, a scale-like low crystallinity silica with the high safety to a human body and its manufacture method will be offered.
[0010]
[Embodiments of the Invention] Hereafter, this invention is explained in detail.
[0011] First, the scale-like silica said to this invention is that in which the primary particle has the configuration of a scale-like

board. 0.001-1 micrometer of thickness is 0.01-0.5 micrometers preferably. the ratio (aspect ratio) of the longest length of a scale-like board to thickness -- at least 10 -- 30 or more preferably The ratios of the minimum length of a scale-like board to 50 or more and thickness are at least 3 and the silica of the shape of a scale which has 20 or more still more preferably ten or more preferably still more preferably.

[0012] In addition, as for the former, 200 or less are [300 or less] preferably practical, and, as for the latter, 100 or less are [150 or less] preferably practical, although especially the upper limit of the ratio of the longest length to thickness and the ratio of the minimum length is not specified.

[0013] Here, that what is necessary is just to carry out the form of a tabular to the scale-like board substantially, partially or on the whole, it may bend, or you may twist. Moreover, the thickness of the silica of the scale-like board of this invention and especially length mean the average about the primary particle, unless it refuses.

[0014] Moreover, the measured value of the crystallized type isolation silicic acid which measured the silica of this invention by the analyzing method which carried out the postscript is still more desirable 2% (below limit-of-detection) and very few scale-like silicas of low crystallinity less than 5% preferably less than 10%.

[0015] In addition, most tailing which the silica of this invention is measurement by the analyzing method, and shows the so-called amorphous state is not observed.

[0016] Furthermore, the silica of this invention is a scale-like silica of low crystallinity which has preferably 3600-3700 of an IR spectrum, and the silanol group which had one absorption band in 3400-3500cm-1, respectively.

[0017] Let a specific ****** silica sol be a start raw material for the source of a silica, and the source of alkali fundamentally in this invention. Especially, they are a silica / alkali mole ratio (Me shows alkali metal, such as Li, Na, or K, SiO2 / Me2 O, and here.). Hereafter, it is the same. The silica sol which carried out dealkalization of the 1.0-3.4 mols [/mol] silicic acid alkali solution by the ion-exchange resin method or the electrodialysis process is used suitably. In addition, as silicic acid alkali solution, what diluted water glass with water suitably, for example is used suitably.

[0018] The silica / alkali mole ratio of the silica sol which is used as a start raw material by this invention in this way and which carried out dealkalization (SiO2 / Me2 O) have the desirable range of 3.5-20 mols/mol, and its range which is 4.5-18 mols/mol is still more desirable. If a mole ratio becomes low, since the solubility of a silica will rise and yield will get worse, it is not so more desirable than this range. On the other hand, if a mole ratio becomes high, since the stability of a silica sol will fall, it is not so more desirable than this range.

[0019] The silica concentration in a silica sol has 2 - 20 desirable % of the weight, and especially its 3 - 15 % of the weight is desirable. Since productivity will fall if concentration is not much lower than this range, it is not desirable. Moreover, since the stability of a silica sol will fall if concentration is not much higher than this range, it is not desirable.

[0020] Although the silica particle diameter in a silica sol means a mean particle diameter and does not limit it especially, its thing 100nm or less is desirable, and especially its so-called active silica 20nm or less is desirable also in it. Moreover, although especially the lower limit of particle size does not limit, a thing 0.5nm or more is desirable. If particle size becomes not much large exceeding 100nm, since the stability of a silica sol will fall, it is not desirable. In addition, although it is not limited especially if the measuring method of a silica particle diameter has a measurable grain size of this range, it can be measured by laser beam dispersion particle-size-analysis equipment, scale measurement of the particle image size photoed with the transmission electron microscope, etc.

[0021] More than solves, a silica sol is used as a start raw material, this is heated in heating pressurized containers, such as an autoclave, hydrothermal processing is performed, and the low crystallinity silica of the shape of a scale made into the purpose is made to generate in this invention.

[0022] In addition, since hydrothermal processing of the silica sol is carried out, it is also possible by preceding teaching an autoclave and adding the purified water like distilled water or ion exchange water further to prepare silica concentration in the range of desired.

[0023] although it is not what limits the form especially as an autoclave -- at least -- a heating means and a stirring means -- and what is necessary is just to have a thermometry means preferably

[0024] In this invention, hydrothermal processing is performed by the 150-250-degree C temperature requirement, and it is 170-220 degrees C preferably. Since a long time will be needed for obtaining the low crystallinity silica of the shape of a scale made into the purpose when temperature is not much lower than this, it is not desirable. On the other hand, since the low crystallinity silica of the shape of a target scale consists of this at an elevated temperature not much that it is hard to be obtained as a single phase, it is not desirable. The low crystallinity silica of the shape of a scale made into the purpose of this invention is considered to be a metastable phase, a place with the inclination which carries out phase transition to a cristobalite and a quartz watch serially with advance of hydrothermal processing, an elevated temperature and when exceeding especially 250 degrees C, the crystallization effect becomes large, and this is considered to be easy to generate mixture with a cristobalite or a quartz watch.

[0025] moreover -- although the time of required hydrothermal processing may change by the temperature of hydrothermal processing, the existence of addition of seed crystal, etc. -- usually -- it is about 5 - 25 hours more preferably for 5 to 40 hours for 5 to 50 hours

[0026] In addition, in this invention, although the addition is not indispensable in order to advance hydrothermal processing efficiently and to shorten the processing time, it is more desirable to add seed crystal. Although the addition of seed crystal is not limited, of course, its about 0.001 - 1 % of the weight is desirable to the charge of the silica sol of a raw material.

[0027] After a hydrothermal processing end, a hydrothermal processing product is taken out from an autoclave, and is filtered and

rinsed. As for the particle after rinsing processing, it is desirable that pH when considering as 10% of the weight of a water slurry is 5-9, and more desirable pH is 6-8.
[0028] Fundamentally, finally the low crystallinity silica of the shape of a scale used by this invention is obtained by drying this. If the cake of this hydrothermal processing product is seen in microscope in the state where it filtered and rinsed, since the portion which forms a floc (aggregated-particle) to which the primary-particle comrade of the shape of each scale adhered will be observed, if needed, this floc can be unfolded before dryness and the operation distributed as a primary particle, i.e., distributed processing, (crack processing) can also be performed. However, since the excellent enough effect is acquired even if it blends the obtained particle with the charge of makeup etc. as it is, without carrying out distributed processing of this case [like the use as powder added to the charge of makeup, an antiperspirant, a pack agent, a paint, or a resin], distributed processing is not necessarily required.
[0029] In addition, especially as a method in the case of performing distributed processing, although it does not limit, the chemical distribution method which used alkali other than the mechanical-dispersion method using the ultrasonic homogenizer, the wet bead mill, etc., such as caustic alkali of sodium and caustic potash, is also effective. So to speak, in order [whose mechanism of a manifestation of the effect in this chemical distribution method exists in the adhesion section of each scale-like particles] for the amount of [as a binder] easy solubility silica to dissolve by addition of this alkali, it is presumed to be what the each first particle separates mutually and distributes.
[0030] In addition, after it washes the dryness operation after distributed processing by low-boiling point organic solvents, such as remaining as it is or an acetone, and a methanol, and it carries out solvent substitution of the attached groundwater, it is performed. Although especially a dryer is not limited, arbitrary equipments, such as a pneumatic conveyor dryer, a fluidized-bed-drying machine, a medium fluidized-bed-drying machine, a stirred type dryer, a cylinder dryer, a compartment dryer, a band dryer, a hot air drying equipment, a vacuum dryer, and an oscillating dryer, are employable. Moreover, as for drying temperature, it is usually desirable to carry out at about 50-300 degrees C.
[0031] Physicochemical analysis of the low crystallinity silica of the shape of a scale which were obtained by carrying out is performed as follows like the above.
[0032] That is, the silanol group which exists in the front face of a low crystallinity silica is called for by the IR spectrum. Moreover, by [which measure thickness, the longest length, and the minimum length] having taken a photograph by the scanning electron microscope, a scale etc. is enough hit against the primary-particle image of the shape of much scale, and an aspect ratio is called for.
[0033] Moreover, crystallized type isolation silicic acid is measured by the analyzing method indicated by the measurement-of-working-environment guidebook (edited one by the mineral dust relation Ministry of Labor Industrial Safety and Health Department environmental improvement room) in accordance with the measurement-of-working-environment criteria shown in the notification about labor security and hygiene law.
[0034]
[Effect of the Invention] Like the above, the primary particle consists of a scale-like board whose thickness is 0.001-1 micrometer, and the low crystallinity silica of the shape of a scale of this invention which were obtained by carrying out excels ratio / of the longest length of a scale-like board] the form of the shape of a scale in which the ratio of the minimum length of a scale-like board to at least 10 and thickness has at least 3 in properties, such as nothing, spreading nature, a stacking tendency, and concealment nature,.
[0035] Moreover, it sets to the low crystallinity silica of the shape of a scale of this invention. The crystallized type isolation silicic acid used as the cause which causes silicosis Were indicated by the measurement-of-working-environment guidebook edited one by the mineral dust relation Ministry of Labor Industrial Safety and Health Department environmental improvement room) in accordance with the measurement-of-working-environment criteria shown in the notification about labor security and hygiene law. It is displayed with the measured value by the analyzing method, and this value sets a pure quartz watch to 100, and less than 10%, preferably, with 2% (below limit-of-detection), it is very small and it can be said still more preferably that it is very safe for a human body less than 5%.
[0036] Furthermore, the silica of this invention has preferably 3600-3700 of an IR spectrum, and the silanol group which had one absorption band in 3400-3500cm-1, respectively while having the form of the shape of this scale. Therefore, since a silanol group with high reaction activity exists in the front face, the chemical modification by the desired organic component is also possible for this silica.
[0037] Therefore, the low crystallinity silica of the shape of a scale of this invention is a very useful material which can be used suitable for various uses, such as fillers, such as a charge of makeup, an antiperspirant, a pack agent, a paint, and a resin, and chromatography support, a catalyst support.
[0038] Hereafter, an example explains the mode of concrete operation of this invention. Although it is needless to say, these are for clarifying technical meaning of this invention more, and the technical range of this invention is not restrictively interpreted by these.
[0039] In addition, the silanol group in the following examples, an aspect ratio, and the amount of crystallized type isolation silicic acid are calculated by the above-mentioned method. Moreover, that it is only with "%" below shows "weight %."
[0040]
[Example]
[an example 1] -- the autoclave (an electric heating formula --) of capacity 1000cm3 equipped with the heating means and the

stirring means support type impeller [ ] -- a silica sol (composition: -- SiO2 -- 8.5%) 200.73% of Na, SiO2 / Na2 O mole ratio = 12.0 mol /of 470g and 330g of ion exchange water were taught mol, and hydrothermal processing was performed at 200 degrees C for 12 hours, 0.1g having added, having carried out the temperature up of the seed crystal, and stirring by 10rpm.
[0041] In addition, the silica sol of a start raw material diluted JIS No. 3 water glass with water, and electrodialyzed and obtained it, and when the mean particle diameter of the colloid silica in it was measured with the laser beam dispersion particle-size-analysis equipment made from Otsuka Electron, it was 3nm or less.
[0042] Again, after filtration, the ultrasonic homogenizer performed distributed processing for the hydrothermal processing object after filtration and rinsing, and after the acetone replaced attached groundwater, it dried at 180 degrees C for 2 hours, and the 32.5g impalpable powder was obtained.
[0043] When the generation phase was identified for this obtained impalpable powder by the powder X diffraction spectrum, it turns out that it is the single phase of the silica X characterized by the peak (2theta=4.9 degree and 26.0 degrees).
[0044] Moreover, it was checked that the scanning-electron-microscope observation of this impalpable powder of the particle shape of the primary particle is also a scale-like. For the average longest length of a board [as opposed to this thickness to 0.05 micrometers in average thickness of this scale-like particle], the aspect ratio was [the aspect ratio of 60 and the average minimum length of a board] 24 in 1.2 micrometers at 3 micrometers.
[0045] In addition, one existed in 3600-3700cm-1 and, as for the IR spectrum, one absorption band existed in 3400-3500cm-1. This IR chart was shown in drawing 1 of an accompanying drawing.
[0046] Furthermore, when the amount of crystallized type isolation silicic acid of this impalpable powder was measured, it turns out that it is below limit of detection (less than [2%]).
[0047] [an example 2] -- the autoclave (an electric heating formula --) of capacity 1000cm3 equipped with the same heating means as an example 1, and the stirring means support type impeller [ ] -- a silica sol (composition: -- SiO -- 28.5%) 200.73% of Na, SiO2 / Na2 O mole ratio = 12.0 mol /of 470g and 330g of ion exchange water were taught mol, and hydrothermal processing was performed at 180 degrees C for 24 hours, 0.1g having added, having carried out the temperature up of the seed crystal, and stirring by 10rpm.
[0048] The silica sol of a start raw material was prepared like the example 1, and when the mean particle diameter of the colloid silica in it was measured with the transmission electron microscope, it was about 2-5nm.
[0049] Again, after filtration, the ultrasonic homogenizer performed distributed processing for the hydrothermal processing object after filtration and rinsing, and after the acetone replaced attached groundwater, it dried like the example 1, and the 32.3g impalpable powder was obtained.
[0050] When the generation phase was identified for this obtained impalpable powder by the powder X diffraction spectrum, it turns out like an example 1 that it is the single phase of Silica X.
[0051] Moreover, it was checked that the scanning-electron-microscope observation of this impalpable powder of the particle shape of the primary particle is also a scale-like. For the average longest length of a board [as opposed to this thickness to 0.04 micrometers in average thickness of this scale-like particle], the aspect ratio was [the aspect ratio of 100 and the average minimum length of a board] 38 in 1.5 micrometers at 4 micrometers.
[0052] In addition, the position of an absorption band and the number of the IR spectrum were the same as that of an example 1.
[0053] Furthermore, when the amount of crystallized type isolation silicic acid of this impalpable powder was measured, it turns out that it is below limit of detection (less than [2%]).
[0054] [an example 3] -- the autoclave (an electric heating formula --) of capacity 1000cm3 equipped with the same heating means as an example 1, and the stirring means support type impeller [ ] -- a silica sol (composition: -- SiO -- 210.0%) 202.08% of Na, SiO2 / Na2 O mole ratio = 5.0 mol /of 400g and 400g of ion exchange water were taught mol, and hydrothermal processing was performed at 200 degrees C for 10 hours, 0.1g having added, having carried out the temperature up of the seed crystal, and stirring by 10rpm.
[0055] The silica sol of a start raw material was prepared like the example 1, and when the mean particle diameter of the colloid silica in it was measured as well as the example 1 with the laser beam dispersion particle-size-analysis equipment made from Otsuka Electron, it was 3nm or less.
[0056] Again, after filtration, the ultrasonic homogenizer performed distributed processing for the hydrothermal processing object after filtration and rinsing, and after the acetone replaced attached groundwater, it dried like the example 1, and the 28.5g impalpable powder was obtained.
[0057] When the generation phase was identified for this obtained impalpable powder by the powder X diffraction spectrum, it turns out like an example 1 that it is the single phase of Silica X.
[0058] Moreover, it was checked that the scanning-electron-microscope observation of this impalpable powder of the particle shape of the primary particle is also a scale-like. For the average longest length of a board [as opposed to this thickness to 0.05 micrometers in average thickness of this scale-like particle], the aspect ratio was [the aspect ratio of 80 and the average minimum length of a board] 24 in 1.2 micrometers at 4 micrometers.
[0059] In addition, the position of an absorption band and the number of the IR spectrum were the same as that of an example 1.
[0060] Furthermore, when the amount of crystallized type isolation silicic acid of this impalpable powder was measured, it turns out that it is below limit of detection (less than [2%]).
[0061] [an example 4] -- the autoclave (an electric heating formula --) of capacity 1000cm3 equipped with the same heating means as an example 1, and the stirring means support type impeller [ ] -- a silica sol (composition: -- SiO -- 213.5%) 203.98%

of Na, SiO2 / Na2 O mole ratio = 3.5 mol /of 296g and 504g of ion exchange water were taught mol, and hydrothermal processing was performed at 200 degrees C for 8 hours, 0.1g having added, having carried out the temperature up of the seed crystal, and stirring by 10rpm.
[0062] The silica sol of a start raw material was prepared like the example 1, and when the mean particle diameter of the colloid silica in it was measured as well as the example 1 with the laser beam dispersion particle-size-analysis equipment made from Otsuka Electron, it was 3nm or less.
[0063] Again, after filtration, the ultrasonic homogenizer performed distributed processing for the hydrothermal processing object after filtration and rinsing, and after the acetone replaced attached groundwater, it dried like the example 1, and the 15.6g impalpable powder was obtained.
[0064] When the generation phase was identified for this obtained impalpable powder by the powder X diffraction spectrum, it turns out like an example 1 that it is the single phase of Silica X.
[0065] Moreover, it was checked that the scanning-electron-microscope observation of this impalpable powder of the particle shape of the primary particle is also a scale-like. For the average longest length of a board [as opposed to this thickness to 0.05 micrometers in average thickness of this scale-like particle], the aspect ratio was [the aspect ratio of 100 and the average minimum length of a board] 10 in 0.5 micrometers at 5 micrometers.
[0066] In addition, the position of an absorption band and the number of the IR spectrum were the same as that of an example 1.
[0067] Furthermore, when the amount of crystallized type isolation silicic acid of this impalpable powder was measured, it turns out that it is below limit of detection (less than [2%]).
[0068] [an example 5] -- the autoclave (an electric heating formula --) of capacity 1000cm3 equipped with the same heating means as an example 1, and the stirring means support type impeller [ ] -- a silica sol (composition: -- SiO -- 28.5%) 200.73% of Na, SiO2 / Na2 O mole ratio = 12.0 mol /of 470g and 330g of ion exchange water were taught mol, and seed crystal performed hydrothermal processing at 200 degrees C for 36 hours, having carried out the temperature up and stirring by 10rpm without adding.
[0069] The silica sol of a start raw material was prepared like the example 1, and when the mean particle diameter of the colloid silica in it was measured as well as the example 1 with the laser beam dispersion particle-size-analysis equipment made from Otsuka Electron, it was 3nm or less.
[0070] Again, after filtration, the ultrasonic homogenizer performed distributed processing for the hydrothermal processing object after filtration and rinsing, and after the acetone replaced attached groundwater, it dried like the example 1, and the 32.0g impalpable powder was obtained.
[0071] When the generation phase was identified for this obtained impalpable powder by the powder X diffraction spectrum, it turns out like an example 1 that it is the single phase of Silica X.
[0072] Moreover, it was checked that the scanning-electron-microscope observation of this impalpable powder of the particle shape of the primary particle is also a scale-like. For the average longest length of a board [as opposed to this thickness to 0.06 micrometers in average thickness of this scale-like particle], the aspect ratio was [the aspect ratio of 83 and the average minimum length of a board] 25 in 1.5 micrometers at 5 micrometers.
[0073] In addition, the position of an absorption band and the number of the IR spectrum were the same as that of an example 1.
[0074] Furthermore, when the amount of crystallized type isolation silicic acid of this impalpable powder was measured, it turns out that it is below limit of detection (less than [2%]).
[0075] [Example 6] After the acetone replaced attached groundwater, without having performed hydrothermal processing on the same conditions as an example 1, and performing distributed processing (crack processing) for the obtained hydrothermal processing object after filtration and rinsing, it dried like the example 1, and the 32.8g impalpable powder was obtained.
[0076] When the generation phase was identified for this obtained impalpable powder by the powder X diffraction spectrum, it turns out that it is the single phase of Silica X like an example 1.
[0077] Moreover, in scanning-electron-microscope observation of this impalpable powder, the portion which forms a floc to which the scale-like primary-particle comrade adhered was accepted considerably. For the average longest length of a board [as opposed to this thickness to 0.06 micrometers in average thickness of the primary particle of the shape of this scale], the aspect ratio was [the aspect ratio of 50 and the average minimum length of a board] 25 in 1.5 micrometers at 3 micrometers.
[0078] Moreover, one existed in 3600-3700cm-1 and, as for the IR spectrum, one absorption band existed in 3400-3500cm-1.
[0079] Furthermore, when the amount of crystallized type isolation silicic acid of this impalpable powder was measured, it turns out that it is below limit of detection (less than [2%]).
[0080] [Example 7] After the acetone replaced attached groundwater, without having performed hydrothermal processing on the same conditions as an example 2, and performing distributed processing (crack processing) for the obtained hydrothermal processing object after filtration and rinsing, it dried like the example 2, and the 32.5g impalpable powder was obtained.
[0081] When the generation phase was identified for this obtained impalpable powder by the powder X diffraction spectrum, it turns out that it is the single phase of Silica X like an example 2.
[0082] Moreover, in scanning-electron-microscope observation of this impalpable powder, the portion which forms a floc to which the scale-like primary-particle comrade adhered was accepted considerably. For the average longest length of a board [as opposed to this thickness to 0.05 micrometers in average thickness of the primary particle of the shape of this scale], the aspect ratio was [the aspect ratio of 80 and the average minimum length of a board] 30 in 1.5 micrometers at 4 micrometers.
[0083] In addition, the position of an absorption band and the number of the IR spectrum were the same as that of an example 2.

[0084] Furthermore, when the amount of crystallized type isolation silicic acid of this impalpable powder was measured, it turns out that it is below limit of detection (less than [2%]).
[0085] [Example 8] After the acetone replaced attached groundwater, without having performed hydrothermal processing on the same conditions as an example 3, and performing distributed processing (crack processing) for the obtained hydrothermal processing object after filtration and rinsing, it dried like the example 3, and the 28.6g impalpable powder was obtained.
[0086] When the generation phase was identified for this obtained impalpable powder by the powder X diffraction spectrum, it turns out that it is the single phase of Silica X like an example 3.
[0087] Moreover, in scanning-electron-microscope observation of this impalpable powder, the portion which forms a floc to which the scale-like primary-particle comrade adhered was accepted considerably. For the average longest length of a board [as opposed to this thickness to 0.05 micrometers in average thickness of the primary particle of the shape of this scale], the aspect ratio was [the aspect ratio of 80 and the average minimum length of a board] 26 in 1.3 micrometers at 4 micrometers.
[0088] In addition, the position of an absorption band and the number of the IR spectrum were the same as that of an example 1.
[0089] Furthermore, when the amount of crystallized type isolation silicic acid of this impalpable powder was measured, it turns out that it is below limit of detection (less than [2%]).
[0090] [Example 9] After the acetone replaced attached groundwater, without having performed hydrothermal processing on the same conditions as an example 4, and performing distributed processing (crack processing) for the obtained hydrothermal processing object after filtration and rinsing, it dried like the example 4, and the 15.5g impalpable powder was obtained.
[0091] When the generation phase was identified for this obtained impalpable powder by the powder X diffraction spectrum, it turns out that it is the single phase of Silica X like an example 4.
[0092] Moreover, in scanning-electron-microscope observation of this impalpable powder, the portion which forms a floc to which the scale-like primary-particle comrade adhered was accepted considerably. For the average longest length of a board [as opposed to this thickness to 0.05 micrometers in average thickness of the primary particle of the shape of this scale], the aspect ratio was [the aspect ratio of 100 and the average minimum length of a board] 10 in 0.5 micrometers at 5 micrometers.
[0093] In addition, the position of an absorption band and the number of the IR spectrum were the same as that of an example 1.
[0094] Furthermore, when the amount of crystallized type isolation silicic acid of this impalpable powder was measured, it turns out that it is below limit of detection (less than [2%]).
[0095] [Example 10] After the acetone replaced attached groundwater, without having performed hydrothermal processing on the same conditions as an example 5, and performing distributed processing (crack processing) for the obtained hydrothermal processing object after filtration and rinsing, it dried like the example 5, and the 32.2g impalpable powder was obtained.
[0096] When the generation phase was identified for this obtained impalpable powder by the powder X diffraction spectrum, it turns out that it is the single phase of Silica X like an example 5.
[0097] Moreover, in scanning-electron-microscope observation of this impalpable powder, the portion which forms a floc to which the scale-like primary-particle comrade adhered was accepted considerably. For the average longest length of a board [as opposed to this thickness to 0.06 micrometers in average thickness of the primary particle of the shape of this scale], the aspect ratio was [the aspect ratio of 83 and the average minimum length of a board] 20 in 1.2 micrometers at 5 micrometers.
[0098] In addition, the position of an absorption band and the number of the IR spectrum were the same as that of an example 1.
[0099] Furthermore, when the amount of crystallized type isolation silicic acid of this impalpable powder was measured, it turns out that it is below limit of detection (less than [2%]).
[0100] As mentioned above, it was checked by using a silica sol as a start raw material, and performing hydrothermal processing that the low crystallinity silica of the shape of a scale which has a silanol group to the sufficiently few specific field of an IR spectrum of the content of crystallized type isolation silicic acid which is the specified substance of this invention is generated so that clearly from an example.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the IR-spectrum chart of the silica obtained in the example 1.

[Translation done.]

* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] The scale-like silica of low crystallinity thin [from the scale-like board which is 0.001-1 micrometer] and characterized by for the ratio (aspect ratio) of the longest length of this scale-like board to this thickness being the silica of the shape of a scale in which the ratio of the minimum length of this scale-like board to at least 10 and this thickness has at least 3, and the measured value of the crystallized type isolation silicic acid by the analyzing method being less than 10%.
[Claim 2] 3600-3700 of an IR spectrum, the scale-like silica of low crystallinity according to claim 1 characterized by having the silanol group which had one absorption band in 3400-3500cm-1, respectively.
[Claim 3] The manufacture method of the scale-like silica of low crystallinity according to claim 1 or 2 which uses as a start raw material the silica sol obtained by carrying out dealkalization of the silicic acid alkali solution, carries out hydrothermal processing of this silica sol, and is characterized by the bird clapper.
[Claim 4] The manufacture method of a scale-like silica according to claim 3 that the silica / alkali mole ratio of a silica sol (SiO2 / Me2 O, Me indicates alkali metal to be here) are characterized by being 3.5 mols/mol - 20 mols/mol.
[Claim 5] The manufacture method of the scale-like silica according to claim 3 or 4 characterized by the silica particle diameter of a silica sol being 100nm or less.
[Claim 6] The manufacture method of the scale-like silica according to claim 3 to 5 characterized by adding seed crystal in the case of hydrothermal processing.

[Translation done.]

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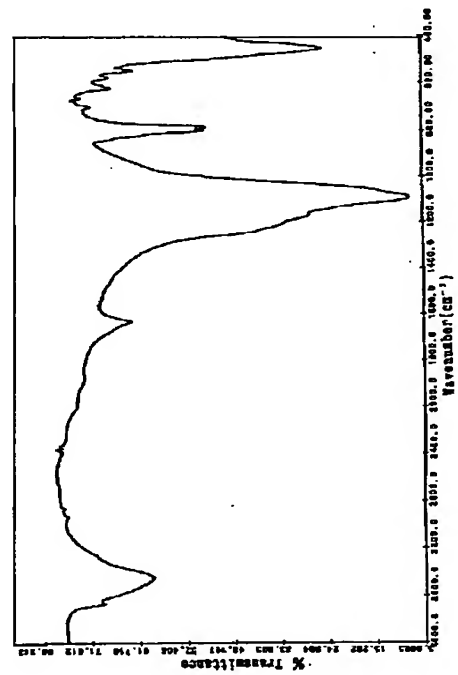
最終頁に続く

(54)【発明の名称】　鱗片状の低結晶性シリカとその製造方法

(57)【要約】

【課題】　人体に無害であり、表面の反応性に優れる、化粧料、制汗剤、パック剤、塗料もしくは樹脂などのフィラーや各種担体等の用途に好適に使用できる、鱗片状の低結晶性シリカ及びその製造方法を提供する。

【解決手段】　厚さ０．００１～１μｍ、厚さに対する鱗片状板の最長長さの比（アスペクト比）１０以上、厚さに対する鱗片状板の最小長さの比３以上の鱗片状のシリカで、結晶型遊離珪酸の測定値１０％未満、ＩＲスペクトルの３６００～３７００、３４００～３５００ｃｍ$^{-1}$にシラノール基の吸収を有する低結晶性の鱗片状シリカ及び珪酸アルカリ水溶液を脱アルカリして得られるシリカゾルを水熱処理するその製造方法。



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【特許請求の範囲】

【請求項1】　厚さが0．001～1μmの鱗片状板からなり、該厚さに対する該鱗片状板の最長長さの比（アスペクト比）が少なくとも10、該厚さに対する該鱗片状板の最小長さの比が少なくとも3を有する鱗片状のシリカであって、かつ、X線回折分析法による結晶型遊離珪酸の測定値が10%未満であることを特徴とする低結晶性の鱗片状シリカ。

【請求項2】　IRスペクトルの3600～3700、3400～3500cm^{-1}にそれぞれ1つの吸収帯を持ったシラノール基を有することを特徴とする請求項1記載の低結晶性の鱗片状シリカ。

【請求項3】　珪酸アルカリ水溶液を脱アルカリして得られるシリカゾルを出発原料とし、該シリカゾルを水熱処理せしめてなることを特徴とする請求項1または2記載の低結晶性の鱗片状シリカの製造方法。

【請求項4】　シリカゾルのシリカ／アルカリモル比（SiO_2／Me_2O、ここでMeはアルカリ金属を示す）が、3．5mol／mol～20mol／molであることを特徴とする請求項3記載の鱗片状シリカの製造方法。

【請求項5】　シリカゾルのシリカ粒子径が100nm以下であることを特徴とする請求項3または4記載の鱗片状シリカの製造方法。

【請求項6】　水熱処理の際に、種晶を添加することを特徴とする請求項3～5のいずれかに記載の鱗片状シリカの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、人体に無害である一方、表面の反応性に優れ、化粧料、制汗剤、パック剤、塗料もしくは樹脂などのフィラーやクロマトグラフィー担体および触媒担体等の用途に好適に使用できる、鱗片状の低結晶性シリカ及びその製造方法に関するものである。

【0002】

【従来の技術】従来、所謂シリカXとよばれる、X線回折でピークがでるという意味においての結晶質シリカが知られている（Beitr.Mineral.Petrogr.10,242-259（1964））。

【0003】これらは、多数の鱗片状粒子が凝着したような形態になっているものの、無孔質でかつ反応性に乏しく、これに特定の物質を担持させたりフィラーとして使用することは実質上困難である。

【0004】また、石英やクリストバライトなどの結晶性シリカは、結晶型遊離珪酸に分類され、粉塵として長期間、人肺に吸入された場合、肺臓およびその周囲組織に沈着し治療が困難な疾病である珪肺（Silicosis）を引き起こす原因となることが病理学的にも確認されており、労働安全衛生面上、じん肺法やじん肺法施行規則に

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おいて規制されている。いっぽう、シリカゲル等の非晶質シリカは非晶型遊離珪酸に分類されるが、非晶型は結晶型に比較して珪肺を引き起こす可能性は著しく小さいことも知られている（粉体と工業,10,25-40（1980））。

【0005】遊離珪酸とは、珪酸塩を構成する結合珪酸と区別した名称で、珪素が酸素とのみ三次元的に結合しており、その他の元素とは結合していない状態であり、要するに二酸化珪素（SiO_2）を意味する。このような遊離珪酸は、上述の非晶型や結晶型等に分類されるが、このうち、珪肺を引き起こす原因となる結晶型の遊離珪酸は、X線回折分析法等により定量が可能である。

【0006】

【発明が解決しようとする課題】本発明の目的は、鱗片状の形態をなすため展着性、配向性、隠蔽性などの特性に優れ、また、労働安全衛生の面から有害な結晶型遊離珪酸の量が充分少なく、さらに、表面に化学修飾が可能な反応性の高い基を有する、新規な低結晶性の鱗片状シリカ及びその製造方法を提供することにある。

【0007】

【課題を解決するための手段】本発明者らは、上記課題の重要性に鑑み鋭意検討した結果、シリカ源およびアルカリ源を含有した出発原料を水熱処理することにより、人体に有害な結晶型遊離珪酸の含有量の充分少ない、鱗片状の低結晶性シリカが得られること、さらに好ましくは、このようにして、鱗片状の低結晶性シリカであってIRスペクトルの特定領域に吸収帯のあるシラノール基を有するものが得られることを見出し、本発明を完成するに到った。

【0008】すなわち、本発明の上記課題は、（1）厚さが0．001～1μmの鱗片状板からなり、該厚さに対する該鱗片状板の最長長さの比（アスペクト比）が少なくとも10、該厚さに対する該鱗片状板の最小長さの比が少なくとも3を有する鱗片状のシリカであって、かつ、X線回折分析法による結晶型遊離珪酸の測定値が10%未満であることを特徴とする低結晶性の鱗片状シリカ、及び、（2）珪酸アルカリ水溶液を脱アルカリして得られるシリカゾルを出発原料とし、該シリカゾルを水熱処理せしめてなることを特徴とする（1）記載の低結晶性の鱗片状シリカの製造方法、によって解決される。

【0009】すなわち、本発明に従えば、人体への安全性の高い、鱗片状の低結晶性シリカ及びその製造方法が提供されるのである。

【0010】

【発明の実施の形態】以下、本発明について詳細に説明する。

【0011】まず、本発明にいう鱗片状シリカは、その一次粒子が鱗片状板の形状を有するもので、厚さが0．001～1μm、好ましくは0．01～0．5μmであり、厚さに対する鱗片状板の最長長さの比（アスペクト比）が少なくとも10、好ましくは30以上、さらに好

ましくは５０以上、厚さに対する鱗片状板の最小長さの比が少なくとも３、好ましくは１０以上、さらに好ましくは２０以上を有するような鱗片状のシリカである。

【００１２】なお、厚さに対する最長長さの比および最小長さの比の上限は特に規定するものではないが、前者は３００以下、好ましくは２００以下が実際的であり、後者は１５０以下、好ましくは１００以下が実際的である。

【００１３】ここで、鱗片状板とは、実質的に板状の形をしていればよく、部分的または全体的に曲がったり、ねじれたりしていてもよい。また、本発明の鱗片状板のシリカの厚さ、長さは特に断らない限り、その一次粒子についての平均値を意味する。

【００１４】また、本発明のシリカは、後記したＸ線回折分析法により測定した、結晶型遊離珪酸の測定値が１０％未満、好ましくは５％未満、さらに好ましくは２％（検出限界以下）と、きわめてわずかな低結晶性の鱗片状シリカである。

【００１５】なお、本発明のシリカは、Ｘ線回折分析法による測定で、所謂アモルファス状態を示すテーリングはほとんど観察されない。

【００１６】さらに本発明のシリカは、好ましくは、ＩＲスペクトルの３６００～３７００、３４００～３５００cm^{-1}にそれぞれ１つの吸収帯を持ったシラノール基を有する低結晶性の鱗片状シリカである。

【００１７】本発明においては、基本的に、シリカ源及びアルカリ源を特定量含むシリカゾルを出発原料とする。特に、シリカ／アルカリモル比（SiO_2／Me_2O、ここでＭｅはＬｉ、ＮａまたはＫなどのアルカリ金属を示す。以下、同じ。）が、１．０～３．４ｍｏｌ／ｍｏｌの珪酸アルカリ水溶液を、イオン交換樹脂法あるいは電気透析法などによって脱アルカリしたシリカゾルが好適に使用される。なお、珪酸アルカリ水溶液としては、たとえば水ガラスを適宜水で希釈したものなどが好適に使用される。

【００１８】かくして本発明で出発原料として使用する脱アルカリしたシリカゾルのシリカ／アルカリモル比（SiO_2／Me_2O）は、３．５～２０ｍｏｌ／ｍｏｌの範囲が好ましく、４．５～１８ｍｏｌ／ｍｏｌの範囲がさらに好ましい。この範囲よりあまりモル比が低くなると、シリカの溶解度が上昇し、収率が悪化するので好ましくない。一方、この範囲よりあまりモル比が高くなると、シリカゾルの安定性が低下するので好ましくない。

【００１９】シリカゾル中のシリカ濃度は２～２０重量％が好ましく、３～１５重量％が特に好ましい。この範囲より濃度があまり低いと生産性が低下するので好ましくない。また、この範囲より濃度があまり高いとシリカゾルの安定性が低下するので好ましくない。

【００２０】シリカゾル中のシリカ粒子径は、平均粒子径を意味し、特に限定するものではないが１００ｎｍ以下のものが好ましく、そのなかでも２０ｎｍ以下の所謂活性珪酸が特に好ましい。また粒径の下限値は特に限定するものではないが、０．５ｎｍ以上のものが好ましい。粒径が１００ｎｍを超えてあまり大きくなると、シリカゾルの安定性が低下するので好ましくない。なお、シリカ粒子径の測定法は、この範囲の粒度が測定可能なものであれば特に限定するものではないが、レーザー光散乱粒度測定装置や、透過型電子顕微鏡により撮影した粒子像サイズのスケール計測などで測定することができる。

【００２１】本発明においては、以上のごときシリカゾルを出発原料とし、これを例えばオートクレーブ等の加熱圧力容器中で加熱して水熱処理を行い、目的とする鱗片状の低結晶性シリカを生成せしめる。

【００２２】なお、シリカゾルを水熱処理するため、オートクレーブに仕込むに先立って、さらに蒸留水やイオン交換水のごとき精製水を加えることにより、シリカ濃度を所望の範囲に調製することも可能である。

【００２３】オートクレーブとしては特にその形式を限定するものではないが、少なくとも加熱手段と撹拌手段及び好ましくは温度測定手段を備えたものであればよい。

【００２４】本発明において水熱処理は１５０～２５０℃の温度範囲で行われ、好ましくは１７０～２２０℃である。これよりあまり温度が低いと、目的とする鱗片状の低結晶性シリカを得るのに長時間を必要とすることになるので好ましくない。一方、これよりあまり高温では、目標とする鱗片状の低結晶性シリカが単一相として得られにくくなるので好ましくない。これは、本発明の目的とする鱗片状の低結晶性シリカが準安定相と考えられ、水熱処理の進行とともに、逐次クリストバライト、クオーツに相転移する傾向があるところ、高温、特に２５０℃を超えるような場合は、結晶化効果が大きくなり、クリストバライトやクオーツとの混合物が生成しやすいためであると考えられる。

【００２５】また、必要な水熱処理の時間は、水熱処理の温度や種晶の添加の有無等により変わりうるが、通常、５～５０時間、好ましくは、５～４０時間、より好ましくは５～２５時間程度である。

【００２６】なお、本発明においては、水熱処理を効率よく進め、処理時間を短くするためには、その添加は必須ではないが、種晶を添加することがより好ましい。種晶の添加量は、もちろん限定するものではないが、原料のシリカゾルの仕込み量に対して０．００１～１重量％程度が好ましい。

【００２７】水熱処理終了後、水熱処理生成物をオートクレーブより取り出し、沪過、水洗する。水洗処理後の粒子は、１０重量％の水スラリーとしたときのｐＨが５～９であることが好ましく、より好ましいｐＨは６～８

である。

【0028】基本的には、これを乾燥することにより、本発明で使用する鱗片状の低結晶性シリカが最終的に得られる。この水熱処理生成物のケーキを、沪過・水洗した状態において顕微鏡的に見ると、個々の鱗片状の一次粒子同志が癒着したような凝集粒子(二次粒子)を形成している部分が観察されるので、必要に応じ、乾燥前に該凝集粒子をほぐし、一次粒子として分散させる操作、すなわち、分散処理(解砕処理)を行うこともできる。ただし、化粧料、制汗剤、パック剤、塗料もしくは樹脂等に添加する粉末としての用途のような場合は、これを分散処理することなく、得られた粒子をそのまま化粧料等に配合しても、十分優れた効果が得られるので、分散処理は必ずしも必要ではない。

【0029】なお、分散処理を行う場合の方法としては、特に限定するものではないが、超音波ホモジナイザーや湿式ビーズミル等を用いた機械的分散方法の他に、苛性ソーダや苛性カリ等のアルカリを用いた化学的分散方法も有効である。この化学的分散方法におけるその効果の発現のメカニズムは、各鱗片状粒子同士の癒着部に存在する言わばバインダーとしての易溶解性シリカ分が、該アルカリの添加により溶解するため、各一次粒子が互いに分離し、分散するものと推定される。

【0030】なお、分散処理後の乾燥操作はそのまま、または、アセトンやメタノール等の低沸点有機溶媒で洗浄して付着水を溶媒置換した後行われる。乾燥装置は特に限定するものではないが、気流乾燥機、流動層乾燥機、媒体流動層乾燥機、撹拌型乾燥機、円筒乾燥機、箱型乾燥機、バンド乾燥機、熱風乾燥機、真空乾燥機、振動乾燥機等任意の装置を採用できる。また、乾燥温度は通常、50～300℃程度で行うのが好ましい。

【0031】以上のごとくして得られた鱗片状の低結晶性シリカの物理化学的分析は以下のようにして行われる。

【0032】すなわち、低結晶性シリカの表面に存在するシラノール基はIRスペクトルにより求められる。また、アスペクト比は走査型電子顕微鏡により撮影された充分多数の鱗片状の一次粒子像にスケール等をあてて、厚さ、最長長さ、最小長さを測定することにより求められる。

【0033】また、結晶型遊離珪酸は、労働安全衛生法に関する告示に示された作業環境測定基準に則る作業環境測定ガイドブック(鉱物性粉塵関係　労働省安全衛生部環境改善室編)に記載された、X線回折分析法により測定される。

【0034】

【発明の効果】以上のごとくして得られた本発明の鱗片状の低結晶性シリカは、その一次粒子が、厚さが0.001～1μmの鱗片状板からなり、厚さに対する鱗片状板の最長長さの比(アスペクト比)が少なくとも10、厚さに対する鱗片状板の最小長さの比が少なくとも3を有する鱗片状の形態をなし、展着性、配向性、隠蔽性などの特性にすぐれる。

【0035】また、本発明の鱗片状の低結晶性シリカにおいては、珪肺を引き起こす原因となる結晶型の遊離珪酸は、労働安全衛生法に関する告示に示された作業環境測定基準に則る作業環境測定ガイドブック(鉱物性粉塵関係　労働省安全衛生部環境改善室編)に記載された、X線回折分析法による測定値で表示され、この値が純クオーツを100として、10%未満、好ましくは5%未満、さらに好ましくは2%(検出限界以下)と、きわめてわずかであり、きわめて人体に安全といいうるものである。

【0036】さらに、本発明のシリカは、該鱗片状の形態を有するとともに、好ましくは、IRスペクトルの3600～3700、3400～3500cm^{-1}にそれぞれ1つの吸収帯を持ったシラノール基を有する。そのため、該シリカは、その表面に反応活性の高いシラノール基が存在することから、所望の有機成分による化学修飾も可能である。

【0037】よって本発明の鱗片状の低結晶性シリカは、化粧料、制汗剤、パック剤、塗料、樹脂等のフィラーやクロマトグラフィー担体および触媒担体等の種々の用途に好適に利用できる極めて有用な材料である。

【0038】以下、実施例により、本発明の具体的な実施の態様を説明する。いうまでもないが、これらは本発明の技術的意義をより明確にするためのものであり、本発明の技術的範囲がこれらにより制限的に解釈されるものではない。

【0039】なお、以下の実施例における、シラノール基、アスペクト比および結晶型遊離珪酸量は上記方法により求めたものである。また、以下単に「%」とあるのは「重量%」を示す。

【0040】

【実施例】

〔実施例1〕加熱手段および撹拌手段を備えた容積1000cm^3のオートクレーブ(電気加熱式、アンカー型撹拌羽根)にシリカゾル(組成：SiO_2 8.5%、Na_2O 0.73%、SiO_2 /Na_2O モル比＝12.0mol／mol)470gとイオン交換水330gを仕込み、種晶を0.1g添加し、昇温して10rpmで撹拌しながら200℃で12時間水熱処理を行った。

【0041】なお、出発原料のシリカゾルは、JIS3号水ガラスを水で希釈して電気透析して得たものであり、その中のコロイド状シリカの平均粒子径は、大塚電子(株)製のレーザー光散乱粒度測定装置で測定したところ、3nm以下であった。

【0042】水熱処理物を沪過、水洗後、超音波ホモジナイザーで分散処理を行い、再度沪過後、付着水をアセトンで置換してから180℃で2時間乾燥し、32.5

gの微粉末を得た。

【0043】この得られた微粉末を粉末X線回折スペクトルにより生成相の同定を行ったところ、2θ＝4．9°及び26．0°のピークを特徴とするシリカXの単一相であることがわかった。

【0044】また、該微粉末の走査型電子顕微鏡観察でも、その一次粒子の粒子形状は、鱗片状であることが確認された。該鱗片状粒子の平均厚さ0．05μmに対し、該厚さに対する板の平均最長長さは3μmでそのアスペクト比は60、板の平均最小長さは1．2μmでそのアスペクト比は24であった。

【0045】なお、そのIRスペクトルは、3600～3700cm^{-1}に一つ、3400～3500cm^{-1}に一つの吸収帯が存在した。添付図面の図1にこのIRチャートを示した。

【0046】さらに、該微粉末の結晶型遊離珪酸量を測定したところ、検出限界以下（2%未満）であることがわかった。

【0047】〔実施例2〕実施例1と同一の加熱手段および撹拌手段を備えた容積1000cm^3のオートクレーブ（電気加熱式、アンカー型撹拌羽根）にシリカゾル（組成：$SiO_2$8．5%、Na_2O0．73%、SiO_2／Na_2Oモル比＝12．0mol／mol）470gとイオン交換水330gを仕込み、種晶を0．1g添加し、昇温して10rpmで撹拌しながら180℃で24時間水熱処理を行った。

【0048】出発原料のシリカゾルは実施例1と同様にして調製したものであり、その中のコロイド状シリカの平均粒子径は、透過型電子顕微鏡により測定したところ、2～5nm程度であった。

【0049】水熱処理物を沪過、水洗後、超音波ホモジナイザーで分散処理を行い、再度沪過後、付着水をアセトンで置換してから実施例1と同様にして乾燥し、32．3gの微粉末を得た。

【0050】この得られた微粉末を粉末X線回折スペクトルにより生成相の同定を行ったところ、実施例1と同様に、シリカXの単一相であることがわかった。

【0051】また、該微粉末の走査型電子顕微鏡観察でも、その一次粒子の粒子形状は、鱗片状であることが確認された。該鱗片状粒子の平均厚さ0．04μmに対し、該厚さに対する板の平均最長長さは4μmでそのアスペクト比は100、板の平均最小長さは1．5μmでそのアスペクト比は38であった。

【0052】なお、そのIRスペクトルは、吸収帯の位置、数ともに実施例1と同様であった。

【0053】さらに、該微粉末の結晶型遊離珪酸量を測定したところ、検出限界以下（2%未満）であることがわかった。

【0054】〔実施例3〕実施例1と同一の加熱手段および撹拌手段を備えた容積1000cm^3のオートクレーブ（電気加熱式、アンカー型撹拌羽根）にシリカゾル（組成：$SiO_2$10．0%、Na_2O2．08%、SiO_2／Na_2Oモル比＝5．0mol／mol）400gとイオン交換水400gを仕込み、種晶を0．1g添加し、昇温して10rpmで撹拌しながら200℃で10時間水熱処理を行った。

【0055】出発原料のシリカゾルは実施例1と同様にして調製しその中のコロイド状シリカの平均粒子径は、実施例1と同じく大塚電子（株）製のレーザー光散乱粒度測定装置で測定したところ、3nm以下であった。

【0056】水熱処理物を沪過、水洗後、超音波ホモジナイザーで分散処理を行い、再度沪過後、付着水をアセトンで置換してから実施例1と同様にして乾燥し、28．5gの微粉末を得た。

【0057】この得られた微粉末を粉末X線回折スペクトルにより生成相の同定を行ったところ、実施例1と同様に、シリカXの単一相であることがわかった。

【0058】また、該微粉末の走査型電子顕微鏡観察でも、その一次粒子の粒子形状は、鱗片状であることが確認された。該鱗片状粒子の平均厚さ0．05μmに対し、該厚さに対する板の平均最長長さは4μmでそのアスペクト比は80、板の平均最小長さは1．2μmでそのアスペクト比は24であった。

【0059】なお、そのIRスペクトルは、吸収帯の位置、数ともに実施例1と同様であった。

【0060】さらに、該微粉末の結晶型遊離珪酸量を測定したところ、検出限界以下（2%未満）であることがわかった。

【0061】〔実施例4〕実施例1と同一の加熱手段および撹拌手段を備えた容積1000cm^3のオートクレーブ（電気加熱式、アンカー型撹拌羽根）にシリカゾル（組成：$SiO_2$13．5%、Na_2O3．98%、SiO_2／Na_2Oモル比＝3．5mol／mol）296gとイオン交換水504gを仕込み、種晶を0．1g添加し、昇温して10rpmで撹拌しながら200℃で8時間水熱処理を行った。

【0062】出発原料のシリカゾルは実施例1と同様にして調製し、その中のコロイド状シリカの平均粒子径は、実施例1と同じく大塚電子（株）製のレーザー光散乱粒度測定装置で測定したところ、3nm以下であった。

【0063】水熱処理物を沪過、水洗後、超音波ホモジナイザーで分散処理を行い、再度沪過後、付着水をアセトンで置換してから実施例1と同様にして乾燥し、15．6gの微粉末を得た。

【0064】この得られた微粉末を粉末X線回折スペクトルにより生成相の同定を行ったところ、実施例1と同様に、シリカXの単一相であることがわかった。

【0065】また、該微粉末の走査型電子顕微鏡観察でも、その一次粒子の粒子形状は、鱗片状であることが確

認された。該鱗片状粒子の平均厚さ０．０５μmに対し、該厚さに対する板の平均最長長さは５μmでそのアスペクト比は１００、板の平均最小長さは０．５μmでそのアスペクト比は１０であった。

【００６６】なお、そのＩＲスペクトルは、吸収帯の位置、数ともに実施例１と同様であった。

【００６７】さらに、該微粉末の結晶型遊離珪酸量を測定したところ、検出限界以下（２%未満）であることがわかった。

【００６８】〔実施例５〕実施例１と同一の加熱手段および撹拌手段を備えた容積１０００ｃｍ^{3}のオートクレーブ（電気加熱式、アンカー型撹拌羽根）にシリカゾル（組成：$SiO_2$８．５%、Na_2O０．７３%、SiO_2／Na_2Oモル比＝１２．０ｍｏｌ／ｍｏｌ）４７０ｇとイオン交換水３３０ｇを仕込み、種晶は添加せずに、昇温して１０ｒｐｍで撹拌しながら２００℃で３６時間水熱処理を行った。

【００６９】出発原料のシリカゾルは実施例１と同様にして調製し、その中のコロイド状シリカの平均粒子径は、実施例１と同じく大塚電子（株）製のレーザー光散乱粒度測定装置で測定したところ、３ｎｍ以下であった。

【００７０】水熱処理物を沪過、水洗後、超音波ホモジナイザーで分散処理を行い、再度沪過後、付着水をアセトンで置換してから実施例１と同様にして乾燥し、３２．０ｇの微粉末を得た。

【００７１】この得られた微粉末を粉末Ｘ線回折スペクトルにより生成相の同定を行ったところ、実施例１と同様に、シリカＸの単一相であることがわかった。

【００７２】また、該微粉末の走査型電子顕微鏡観察でも、その一次粒子の粒子形状は、鱗片状であることが確認された。該鱗片状粒子の平均厚さ０．０６μmに対し、該厚さに対する板の平均最長長さは５μmでそのアスペクト比は８３、板の平均最小長さは１．５μmでそのアスペクト比は２５であった。

【００７３】なお、そのＩＲスペクトルは、吸収帯の位置、数ともに実施例１と同様であった。

【００７４】さらに、該微粉末の結晶型遊離珪酸量を測定したところ、検出限界以下（２%未満）であることがわかった。

【００７５】〔実施例６〕実施例１と同様の条件で水熱処理を行い、得られた水熱処理物を沪過、水洗後、分散処理（解砕処理）を行うことなく、付着水をアセトンで置換してから実施例１と同様に乾燥し、３２．８ｇの微粉末を得た。

【００７６】この得られた微粉末を粉末Ｘ線回折スペクトルにより生成相の同定を行ったところ、実施例１と同様にシリカＸの単一相であることがわかった。

【００７７】また、該微粉末の走査型電子顕微鏡観察では、鱗片状の一次粒子同志が癒着したような凝集粒子を形成している部分がかなり認められた。該鱗片状の一次粒子の平均厚さ０．０６μmに対し、該厚さに対する板の平均最長長さは３μmでそのアスペクト比は５０、板の平均最小長さは１．５μmでそのアスペクト比は２５であった。

【００７８】また、ＩＲスペクトルは、３６００～３７００ｃｍ$^{-1}$に一つ、３４００～３５００ｃｍ$^{-1}$に一つの吸収帯が存在した。

【００７９】さらに、該微粉末の結晶型遊離珪酸量を測定したところ、検出限界以下（２%未満）であることがわかった。

【００８０】〔実施例７〕実施例２と同様の条件で水熱処理を行い、得られた水熱処理物を沪過、水洗後、分散処理（解砕処理）を行うことなく、付着水をアセトンで置換してから実施例２と同様にして乾燥し、３２．５ｇの微粉末を得た。

【００８１】この得られた微粉末を粉末Ｘ線回折スペクトルにより生成相の同定を行ったところ、実施例２と同様にシリカＸの単一相であることがわかった。

【００８２】また、該微粉末の走査型電子顕微鏡観察では、鱗片状の一次粒子同志が癒着したような凝集粒子を形成している部分がかなり認められた。該鱗片状の一次粒子の平均厚さ０．０５μmに対し、該厚さに対する板の平均最長長さは４μmでそのアスペクト比は８０、板の平均最小長さは１．５μmでそのアスペクト比は３０であった。

【００８３】なお、そのＩＲスペクトルは、吸収帯の位置、数ともに実施例２と同様であった。

【００８４】さらに、該微粉末の結晶型遊離珪酸量を測定したところ、検出限界以下（２%未満）であることがわかった。

【００８５】〔実施例８〕実施例３と同様の条件で水熱処理を行い、得られた水熱処理物を沪過、水洗後、分散処理（解砕処理）を行うことなく、付着水をアセトンで置換してから実施例３と同様に乾燥し、２８．６ｇの微粉末を得た。

【００８６】この得られた微粉末を粉末Ｘ線回折スペクトルにより生成相の同定を行ったところ、実施例３と同様にシリカＸの単一相であることがわかった。

【００８７】また、該微粉末の走査型電子顕微鏡観察では、鱗片状の一次粒子同志が癒着したような凝集粒子を形成している部分がかなり認められた。該鱗片状の一次粒子の平均厚さ０．０５μmに対し、該厚さに対する板の平均最長長さは４μmでそのアスペクト比は８０、板の平均最小長さは１．３μmでそのアスペクト比は２６であった。

【００８８】なお、そのＩＲスペクトルは、吸収帯の位置、数ともに実施例１と同様であった。

【００８９】さらに、該微粉末の結晶型遊離珪酸量を測定したところ、検出限界以下（２%未満）であることが

わかった。

【００９０】〔実施例９〕実施例４と同様の条件で水熱処理を行い、得られた水熱処理物を沪過、水洗後、分散処理（解砕処理）を行うことなく、付着水をアセトンで置換してから実施例４と同様に乾燥し、１５．５ｇの微粉末を得た。

【００９１】この得られた微粉末を粉末Ｘ線回折スペクトルにより生成相の同定を行ったところ、実施例４と同様にシリカＸの単一相であることがわかった。

【００９２】また、該微粉末の走査型電子顕微鏡観察では、鱗片状の一次粒子同志が癒着したような凝集粒子を形成している部分がかなり認められた。該鱗片状の一次粒子の平均厚さ０．０５μｍに対し、該厚さに対する板の平均最長長さは５μｍでそのアスペクト比は１００、板の平均最小長さは０．５μｍでそのアスペクト比は１０であった。

【００９３】なお、そのＩＲスペクトルは、吸収帯の位置、数ともに実施例１と同様であった。

【００９４】さらに、該微粉末の結晶型遊離珪酸量を測定したところ、検出限界以下（２％未満）であることがわかった。

【００９５】〔実施例１０〕実施例５と同様の条件で水熱処理を行い、得られた水熱処理物を沪過、水洗後、分散処理（解砕処理）を行うことなく、付着水をアセトンで置換してから実施例５と同様に乾燥し、３２．２ｇの微粉末を得た。

【００９６】この得られた微粉末を粉末Ｘ線回折スペクトルにより生成相の同定を行ったところ、実施例５と同様にシリカＸの単一相であることがわかった。

【００９７】また、該微粉末の走査型電子顕微鏡観察では、鱗片状の一次粒子同志が癒着したような凝集粒子を形成している部分がかなり認められた。該鱗片状の一次粒子の平均厚さ０．０６μｍに対し、該厚さに対する板の平均最長長さは５μｍでそのアスペクト比は８３、板の平均最小長さは１．２μｍでそのアスペクト比は２０であった。

【００９８】なお、そのＩＲスペクトルは、吸収帯の位置、数ともに実施例１と同様であった。

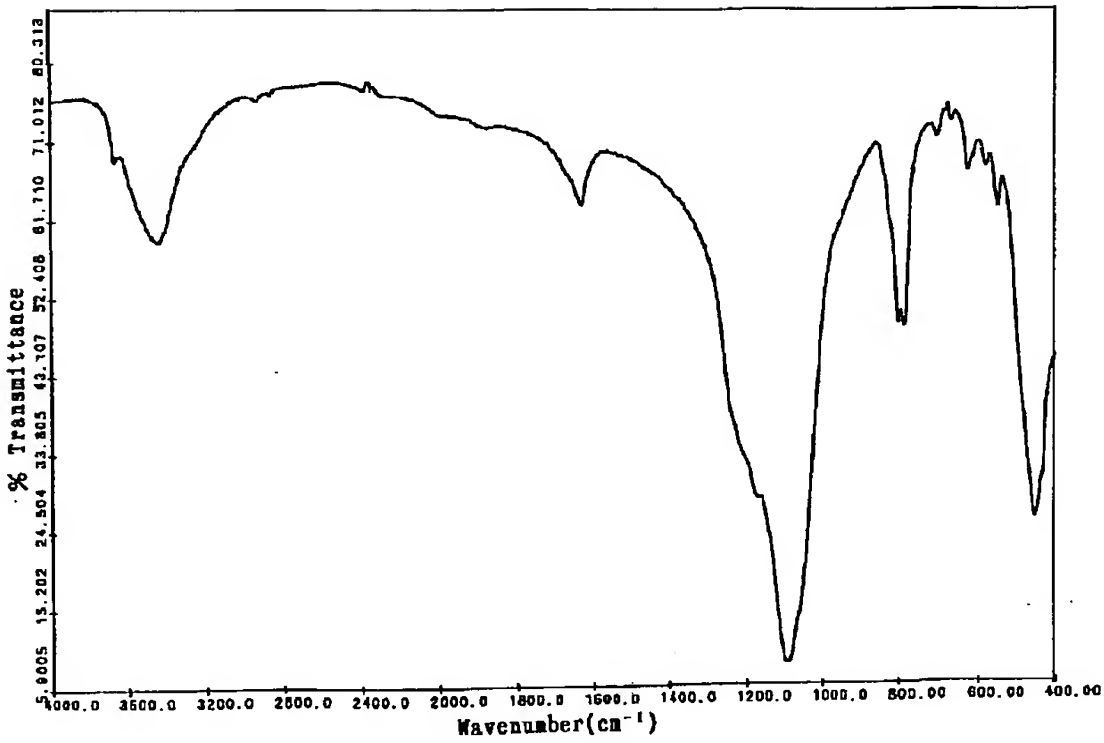
【００９９】さらに、該微粉末の結晶型遊離珪酸量を測定したところ、検出限界以下（２％未満）であることがわかった。

【０１００】以上、実施例から明らかなごとく、シリカゾルを出発原料とし水熱処理を行うことにより、本発明の目的物である、結晶型遊離珪酸の含有量の充分少ない、ＩＲスペクトルの特定領域にシラノール基を有する、鱗片状の低結晶性シリカが生成されることが確認された。

【図面の簡単な説明】

【図１】実施例１で得られたシリカのＩＲスペクトルチャートである。

【図1】



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